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INHIBITORS OF COMBUSTION OF AMMONIUM NITRATE AND AMMONIUM PERCHLORATE AND THEIR MIXTURES

by

A. N. Glazkova and P. P. Popova

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ABSTRACT

The inhibiting effect of ammonium salts, such as ammonium carbonate, oxalate, citrate, tartrate or fluoride, and a reducing agent, such as diphenylamine on the burning rate of ammonium nitrate or ammonium perchlorate was investigated at the Institute of Chemical Physics of the AS USSR. It was announced that the effect of easily dissociating ammonium salts would consist of shifting the equilibrium of the reaction to the left, while the effect of diphenylamine would be either a reduction or a binding of the acid formed in the dissociation, thus inhibiting the further oxidation of ammonia. This assumption was verified experimentally by the combustion of ammatol 80/20 (taken instead of pure ammonium nitrate which does not burn in the bomb) or ammonium perchlorate with or without the additives mentioned above, taken in the amount of 5%; the combustion took place at varying pressures up to 1000 atm in a constant pressure bomb. The best inhibiting effect in the combustion of ammatol 80/20 was obtained with ammonium carbonate. It was observed that the appearance of flame changes depending on the pressure in the bomb: up to 500 atm for addition of ammonium carbonate or oxalate and to 750 atm for ammonium tartrate or citrate. The flame appeared striped, while a uniform flame appeared after this pressure limit; the phenomenon was explained by sedimentation of solid particles, presumably: carbon, on the walls of the vessel. The curve indicating the effect of diphenylamine on the burning rate of ammatol 80/20 rather closely coincided with those of ammonium salts. The ignition of ammatol

80/20 under pressure was delayed to certain initial pressures, e.g., in the presence of $(NH_4)_2 CO_3$ the ignition took place only at 350 atm. The best inhibiting effect on the burning of ammonium perchlorate was exhibited by ammonium fluoride. Ammonium oxalate produced an uneven curve of the rate of combustion. The addition of diphenylamine also produced an uneven rate of combustion; however, the ignition took place without such a considerable delay, without such a dependence or pressure, which was observed for the ammatol with ammonium salts. The effect of diphenylamine on ammonium perchlorate is more pronounced at pressures over 500 atm, which was explained as another mechanism of dissociation ensuing in ammonium perchlorate over their pressure limit. The change in the mechanism of combustion was also confirmed by the changes in the appearance of the photographed flame. Orig. art. has: 4 figures and 2 table.

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В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
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О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

INHIBITORS OF COMBUSTION OF AMMONIUM NITRATE AND AMMONIUM PERCHLORATE AND THEIR MIXTURES

A. N. Glazkova and P. P. Popova

(Submitted 25 Jan. 1967 by Academician N. M. Emanuel)

In certain conditions of application of explosive and mixtures it is necessary to reduce the combustibility and the rate of combustion. Thus, one of the requirements for safety explosives is their low combustibility, which reduces the danger of burnup with failure of detonation, but for mixture fuels reduction of the combustion rate is dictated by the necessity of obtaining compositions with small dependence of combustion rate on pressure (small ν in equation $u = BP^{\nu}$).

Up to now the search for inhibitors of combustion, just as catalysts, carried an especially empirical character. In this work an attempt is made to arrive at the solution of this problem on the basis of the following considerations. It is known that the primary step during thermal dissociation of ammonium nitrate and perchlorate is their dissociation into ammonia and nitric acid during decomposition of nitrate and into ammonia and perchloric acid during decomposition of perchlorate.

If we assume that during combustion of these salts these reactions will be prominent, then for lowering the combustion rate

it is necessary to delay the reaction of further oxidation of ammonia; therefore it is expedient to add substances which possessed either the ability to be easily decomposed during combustion, forming ammonia, or would be reducers.

It is known that the addition of ammonia to ammonium perchlorate delayed its thermal decomposition [1], due to lowering of the rate of formation of radicals ClO_4 (shift of equilibrium to the left), and with its addition to hydrazine the combustion rate of the latter is reduced [2]. Thus, the influence of ammonia in this case is reduced to shift of equilibrium of dissociation to the left, and the influence of substances, possessing reducing properties, will amount to reduction or binding of acids forming during decomposition (or products of their further decomposition) and to slowing further oxidation of ammonia.[1]

For checking this assumption, as substances of the first group there were selected ammonium carbonate, oxalate, citrate, tartrate and fluoride, and as substances of the second group — diphenylamine.

The applied additions, ammonium nitrate and trotyl, had size of particles <100 μ; size of particles of ammonium perchlorate <250 μ.

The inhibiting effect of ammonium oxalate during combustion of ammatol 80/20 in a pressure bomb was established by Andreyev and one of the authors of this article as early as in the Fifties [3]. During the study of combustion of ion-exchange explosives, Nenquin and Fally [4] showed that replacement of ammonium chloride in them by ammonium oxalate led to the fact that the mixture did not ignite at a temperature higher than 300°C.

The influence of the above-indicated additions was studied on an example of combustion of ammatol 80/20[2] and ammonium perchlorate both in pure form and in mixtures. Experiments were conducted in a constant pressure bomb in an atmosphere of nitrogen by the method described earlier [6].

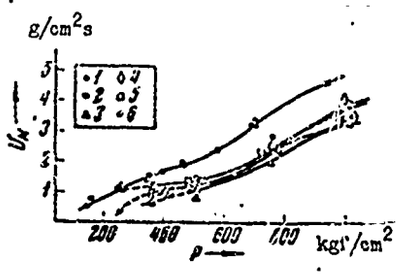

Fig. 1. The effect of inhibitors (10%) on the dependence of combustion rate of ammatol 80/20 on pressure. 1 — pure ammatol, 2 — with ammonium oxalate, 3 — carbonate, 4 — citrate, 5 — tartrate, 6 — with diphenylamine. (Dotted line designates the region of pressures where combustion dies down.)

On the graph of Fig. 1 there are shown the obtained results, and in the same place for comparison there is presented the earlier [6] studied dependence of combustion rate on pressure for pure ammatol 80/20. As can be seen from the graph, ammonium carbonate has the greatest inhibiting action on combustion of ammatol; with its addition the combustion of ammatol dies down in conditions of our experiments even at 350 at , and at 500 at it is delayed by twice as compared to pure ammatol. Slowing of combustion in tne presence of other additions occurs on the average of 1.3-1.6 times at 400 at and 1.5 times at 950 at.[3]

It is interesting to note that the character of combustion in the presence of inhibitors is changed with change of the interval of pressure in which it occurs. In the region of pressures up to 500 at (for example, with the presence of ammonium oxalate and carbonate) or up to 750 at (in the presence of ammonium tartrate or citrate) the flame is characterized by alternating bright flickering horizontal strips, which is connected, as was already noted earlier [7, 8], with deposition on pipe walls of hard unburned particles, in this case, possibly carbon. At higher pressures, 750-1000 at , the flame becomes more uniform.

The inhibiting action of additions is developed to a still greater degree during combustion of ammonium perchlorate. On the graph of Fig. 2 there is shown the dependence of combustion rate on pressure for pure ammonium perchlorate in plexiglas tubes, and also for perchlorate to which there is added 5% ammonium oxalate, diphenylamine, lithium and ammonium fluoride. As was already noted earlier [9], relationship u(p) of ammonium perchlorate has a complex character: in the pressure range above 150 at there is observed drop of the combustion rate with pressure.

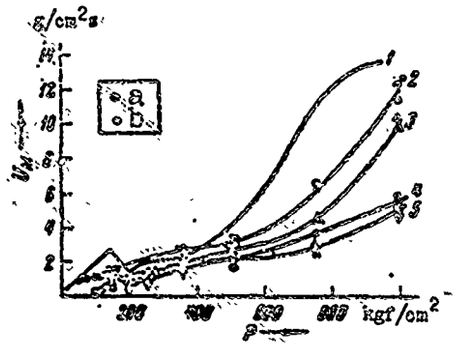

Fig. 2. Dependence of combustion rate of ammonium perchlorate with inhibitors (5%) on pressure. 1 — ammonium perchlorate, 2 — with diphenylamine (a — 1%, b — 5%), 3 — with ammonium oxalate, 4 — with lithium fluoride, 5 — with ammonium fluoride.

With the addition of ammonium oxalate to ammonium perchlorate its combustibility is sharply decreased; at 100 at it does not ignite (pure perchlorate starts to burn at 30 at) and at 150 at burns 3 times slower than pure perchlorate. The combustion rate slowly rises with pressure up to 500-600 at and more sharply with increase of pressure to 1000 at.

Regarding diphenylamine, its addition to perchlorate does not lower combustibility of the latter (mixture starts to burn at pressure ~30 at), however the combustion rate at 150 at , for example, is 2.2 times less than for pure perchlorate; at pressures 200-400 at (in the region of anomalous combustion) the combustion rates coincide, and at pressures higher than 400 at perchlorate with diphenylamine again burns slower than pure (by ~1.5 times). With this we should note that decrease of the amount of diphenylamine to 1% was not reflected on its inhibiting action. As can be seen from the graph of Fig. 2, values of combustion rates both with 5% and with 1% diphenylamine coincide.

Lithium fluoride shows combustion of ammonium perchlorate still more intensely: 5.7 times at 100 at, 3 times at 150 and 2.8 times at 900 at. With this it should be noted that curve u(p) has the same character as for pure ammonium perchlorate. With addition of ammonium fluoride to perchlorate it starts to burn stably only at pressure 300 at, and at 200-250 at combustion dies down; slowing of combustion occurs 2.2 times at pressures up to 500 at and 3.2 times at higher pressures.

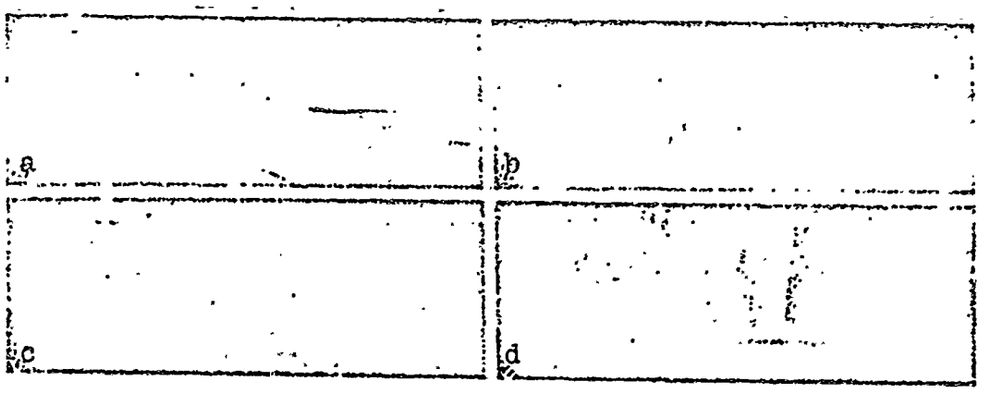

Fig. 3. Photographs of combustion of ammonium perchlorate with diphenylamine at various pressures: a) at 55 at, b) 157 at, c) 505 at, d) 755 at.

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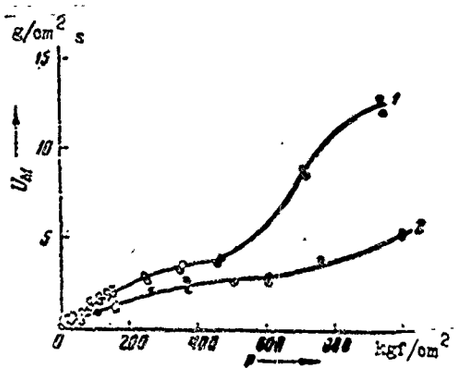

Fig. 4. Effect of lithium fluoride (5%) on combustion of stoichiometric mixture of ammonium perchlorate with coke: 1 — mixture with coke, 2 — the same mixture with lithium fluoride.

Change of the combustion behavior of ammonium perchlorate with the presence of diphenylamine with increase of pressure from 50 to 1000 at can be seen from Fig. 3.

The inhibiting action of additives also appears during combustion of mixtures on an ammonium perchlorate base.

On the graph of Fig. 4 there is shown the dependence of combustion rate on pressure for a stoichiometric mixture of ammonium perchlorate with coke, and also at its pressure with 5% lithium fluoride; the rate is reduced 1.5 times at pressures up to 500 at, 2.7 times at 750 and 2.5 times at 960 at. A similar picture was observed at pressure of 5% $(NH_4)_2C_2O_4$ for stoichiometrical mixture of ammonium perchlorate with fusible monomer (10); lowering of the combustion rate at $\leq$300 at was 1.5 times.

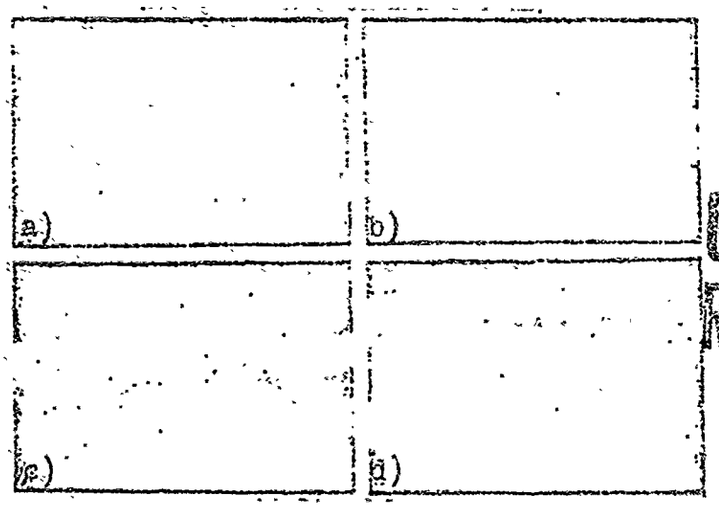

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Fig. 2. Character of destruction of the surface of fiberglass in saturated solution $Ca(OH)_2$, a) after twenty-four hours, b) after 1 month, c) after 3 months, d) characteristic "points" of crystal hydrates on the surface of fiberglass. Filming is in polarized light, 650×.

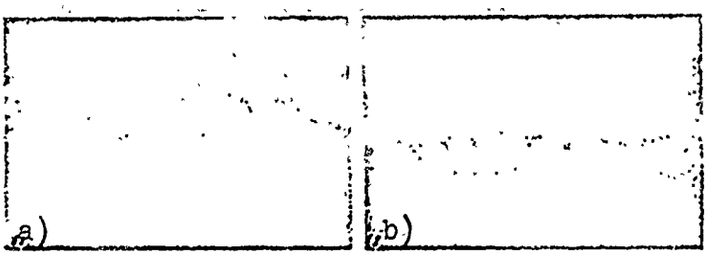

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Fig. 4. Appearance of surface defects of basalt glass fiber, located 2.5 years in cement stone of gypseous-aluminous (a) and aluminous (b) cements. 400×.

Slowing of combustion with the introduction of the studied additives can be connected not only with their influence on the chem. m of reactions, occuring during combustion, but also with ch : of thermochemical parameters, particularly with lowering of 'eat and combustion temperature. Table 1 shows the rated combustion ratures[4] of ammatol 80/20 in pure form and with additions of sa s, applied both in this investigation and earlier (3).

Table 1. Combustion temperature of ammatol 80/20 in pure form and with additives (10%).

Additive	Temp., °C	ΔT
Without additives	2875	—
$(NH_4)_2C_2O_4$	2550	325
$K_2C_2O_4$	2655	220
NaCl	2691	184
KCl	2730	145
NH_4Cl	2589	286

Note: $\Delta T = T_{ammatol}$ minus $T_{ammatol}$ with additive.

GRAPHIC NOT REPRODUCIBLE

From the data of Table 1 it is clear that all additives lower the maximum combustion temperature of ammatol, however, judging by the influence of the studied additives on combustion rate, it is not the determining one. Thus, with the presence of ammonium oxalate, as we have seen above, the combustion rate is decreased, and with the presence of the remaining additives [3, 5, 8], on the contrary, is increased. This indicates that the chemical nature of the additive has a decisive influence, and this may be seen especially clearly during comparison of the influence of oxalates NH_4 and K: with the presence of K, on the contrary, increases 1.5 times, which can serve as confirmation of the correctness of the above-expressed hypothesis. Let us note, incidentally, that the inhibiting action of additives, especially in the case of combustion of ammatol, appears in the entire studied range of pressures, and this can signify that the reaction of dissociation is prominent.

Let us pause further on the inhibiting effect of lithium fluoride on combustion.[5] It is necessary to assume that in this case the delaying mechanism of reactions during combustion is the same, however it is carried out through an intermediate stage: thus, during combustion of ammonium perchlorate with lithium fluoride the latter first interacts with it according to equation:

$$NH_4ClO_4 + LiF = LiClO_4 + NH_4F,$$

and then the forming ammonium fluoride is decomposed into NH_3 and HF:

$$NH_4F \rightarrow NH_3 + HF,$$

which leads to slowing of the combustion process. If this is so, then the direct addition of ammonium fluoride should have a stronger inhibiting action on combustion, since in this case the intermediate stage is excluded, which was indicated above. Actually, from Fig. 2 it is clear that ammonium fluoride is a more effective inhibitor of combustion than LiF.

Finally, we should note distinctions which can be observed, and indeed were observed for various types of inhibitors. Regarding the influence of easily decomposed ammonium salts, their action is equivalent both during combustion of mixtures on an ammonium perchlorate base and nitrate, inasmuch as in this and in other cases in the products of primary decomposition there is contained ammonia.[6] A different picture is observed with the introduction of inhibitors with reducing properties. In a case of combustion of mixtures on an ammonium nitrate base, diphenylamine, for example, can directly affect one of the primary decomposition products — nitric acid; in the case of combustion of mixtures on an ammonium perchlorate base the picture can be changed somewhat. The effect of diphenylamine, as we have seen, appears more intensely at pressures above 500 at, which is apparently connected with decomposition of perchlorate in this region by another mechanism, including the formation of nitrogen oxides, for example [12]:

$$4NH_4ClO_4 = 2Cl_2 + 3O_2 + 8H_2O + 2N_2O \quad \text{or} \quad 2NH_4ClO_4 = 4H_2O + Cl_2 + O_2 + 2NO.$$

The change of combustion mechanism of ammonium perchlorate with the presence of diphenylamine with pressure is also indicated by the change of combustion behavior (see Fig. 3).

Institute of Chemical Physics,
Academy of Sciences of USSR.

Submitted
21 January 1967

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Footnotes

[1]It is necessary to note that ammonia itself possesses reducing properties.

[2]Ammatol 80/20 was taken inasmuch as it makes up the base of industrial explosives, besides pure potassium nitrate in a constant pressure bomb is not combustible [5].

[3]Experiments on determining the influence of diphenylamine on combustion of ammatol 80/20 are conducted by O. K. Andreyev.

[4]Calculations were performed without taking reactions of dissociation into account.

[5]Inhibiting action of lithium fluoride during combustion of perchlorate powders was studied by Horton and Rice [11].

[6]Dissociation of perchlorate with thermal decomposition on the surface during combustion was also assumed by Anderson and Chaiken [13], Inami and others [14].